PB-233 143

METALLIC RECOVERY FROM WASTE WATERS UTILIZING CEMENTATION

Oliver P. Case

Anaconda American Brass Company

Prepared for:

Environmental Protection Agency

January 1974

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

PB 233 143

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

W 74-09062

4. Title
METALLIC RECOVERY FROM WASTE WATERS UTILIZING CEMENTATION,

7. Author(s)
Case, Oliver P.

9. Organization
Engineered Environments Div.
~~Div.~~
Anaconda American Brass Co, Westbury, Connecticut,

10. Project No. EPA Program Element 1BB036

11. ~~Contract~~ Grant No.
S-802254

13. Type of Report and Period Covered

15. Supplementary Notes
Environmental Protection Agency, Technology Series report ~~number~~, EPA-670/2-74-008, January 1974. 36p, 10 fig, 5 tab, 12 ref.

16. Abstract
Bench-scale experiments utilizing the "cementation" reaction (ie electrochemical reduction by contact with a metal of higher oxidation potential) for the precipitation of copper and the reduction of hexavalent chromium in industrial waste streams were performed. Reductants included: soft iron shot 4.37 mm dia, particulate iron approximately -400 mesh and alkali earth metal-silicon alloys in granular form.

Soft iron shot was found to be an effective reductant. Below pH 3.0 chromium reduction is rapid and quantitative. Copper cementation is slower and is influenced more strongly by oxygen, speed of mixing, and available iron surface. Previously deposited copper does not significantly impede further copper deposition. Copper catalyzes the chromium reduction.

Particulate iron was not as satisfactory as the iron shot due to "clumping" of the particles when they became coated with copper.

Silicon alloys were effective for removal of copper, zinc and trivalent chromium, but not reliable for hexavalent chromium since the reaction is not primarily a reducing one. (EPA)

17a. Descriptors
~~Water~~ Pollution Abatement, Chemical ~~Manufacturing~~ Wastes, Industrial Wastes, ~~Metal Finishing Wastes, Material Recovery from Wastewaters, Metal Recovery.~~ Recycling, Waste water treatment, Electrochemistry, Waste treatment, Copper

17b. Identifiers
Copper Recovery, Hexavalent Chromium Reduction, Electrochemical Reduction, Electrochemical Replacement, Cementation, Iron Reductant, Particulate Iron, Alkali Earth Metal-Silicon Alloys, Metal finishing wastes (electrochemical), Metal recovery

17c. COWRR Field & Group 05D

Copy Available from GPO Sup. Doc. as EP1.23:670/2-74-008, microfiche from NTIS as PB 233 143 $1.45

19. Security Class. (Report) $ Unclass
20. Security Class. (Page)
21. No. of Pages 44
22. Price 0.85 - 1.45

Send To:
WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

Reproduced by
NATIONAL TECHNICAL INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

Abstractor Oliver P. Case
Institution Engineered Environments

* U. S. GOVERNMENT PRINTING OFFICE : 1974 731-939/346

EPA-670/2-74-008
January 1974

METALLIC RECOVERY FROM WASTE WATERS UTILIZING CEMENTATION

By

Oliver P. Case

Grant No. S-802254
Program Element 1BB036

Project Officer

Richard Tabakin
Environmental Protection Agency
Edison Water Quality Research Laboratory
National Environmental Research Center
Edison, New Jersey 08817

Prepared for
OFFICE OF RESEARCH AND MONITORING
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Monitoring, Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

EPA REVIEW NOTICE

This report has been reviewed by the Office of Research and Development, EPA, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

This report presents the results of a series of bench-scale experiments utilizing the so-called "cementation" reaction (i.e. electrochemical reduction by contact with a metal of higher oxidation potential) for the precipitation of copper and the reduction of hexavalent chromium in industrial waste streams such as brass mill and metal finishing discharges.

Reductants studied included soft iron shot approximately 4.37 mm dia (0.172 in.), particulate iron (-325 mesh and -400 mesh), and silicon alloys in granular form.

The bulk of the work was done utilizing the iron shot as a reductant. Studies were carried out by both a batch process and a continuous process (back-mix reactor). Results were evaluated in terms of percent reduction, dissolution of excess iron and change in pH vs time.

The particulate iron was studied utilizing batch processes only.

The silicon alloy reductant was studied utilizing both a batch process and a continous process (plug-flow reactor).

This report was submitted in fulfillment of Grant No. S-802254 by the Engineered Environments Division of the Anaconda American Brass Co., under the (partial) sponsorship of the Environmental Protection Agency. Work was completed as of October 1973.

CONTENTS

		Page
Abstract		ii
List of Figures		iv
List of Tables		v
Acknowledgements		vi
Sections		
I	Conclusions	1
II	Recommendations	2
III	Introduction	3
IV	Use of Soft Iron Shot as Reductant	9
V	Use of Particulate Iron as Reductant	23
VI	Use of Silicon Alloys as Reductant	26
VII	References	31
VIII	Appendices	32

FIGURES

No.		Page
1	Reactor Utilized for Reduction Experiments With Iron Shot	10
2	Effect of pH of Feed Solution on Copper Cementation With Iron Shot	12
3	Effect of Oxygen on Copper Cementation With Iron Shot	14
4	Effect of Surface Area of Reductant on Copper Cementation With Iron Shot	15
5	Effect of Previously Deposited Copper on Copper Cementation With Iron Shot	16
6	Reduction of Hexavalent Chromium With Iron Shot	17
7	Simultaneous Cementation of Copper and Reduction of Hexavalent Chromium With Iron Shot	19
8	Effect of Speed of Mixing on Simultaneous Copper Cementation and Reduction of Hexavalent Chromium With Iron Shot	20
9	Continuous Simultaneous Cementation of Copper and Reduction of Hexavalent Chromium With Iron Shot	21
10	Cementation of Copper With Particulate Iron	24

TABLES

No.		Page
1	Metal Removal By Mg-Si Alloy Reacted By Magnetic Stirring	19
2	Metal Removal By Mg-Si Alloy Reacted By Tumbling	20
3	Precipitated Metals Recovered After Reaction of Feed Solution With Mg-Si Alloy	20
4	Metal Removal By Ca-Si Alloy Reacted By Tumbling	21
5	Metal Removal By Mg-Si Alloy Reacted By Continuous Flow	21

ACKNOWLEDGMENTS

Dr. Lawrence C. Kenausis, Assistant Investigator, was helpful in providing information relating to the electro-chemical theory of the cementation reaction and in interpreting experimental results.

Henry A. Agonis, P.E., did a patent search relating to cementation and provided information on commercial systems utilizing the reaction.

David E. Bingham carried out all of the experimental work and provided valuable suggestions on equipment design.

Robert J. Klancko, P.E., provided helpful information on the design of experiments and on the theory of continuous chemical reactions.

SECTION I

CONCLUSIONS

Small diameter iron shot is an effective medium for cementation of copper and reduction of hexavalent chromium, either separately or in a mixture of the two.

Both reactions proceed readily between pH 1.5 and 3.0, but the chromium reduction is much more rapid than the copper cementation.

The chromium reduction is quantitative and the copper cementation nearly so, given enough time.

Exclusion of air makes both reactions more efficient, especially cementation.

The efficiency of cementation is not directly proportional to the available iron surface area.

Increased speed of mixing increases the copper cementation efficiency.

Previously deposited copper does not seriously impede further copper deposition.

Copper apparently catalyzes the reduction of hexavalent chromium and, to a lesser degree, the dissolution of excess iron.

Hexavalent chromium suppresses both copper cementation and dissolution of excess iron to a marked degree.

Particulate iron is effective for cementation of copper, but is difficult to disperse in the feed solution because of "clumping" as soon as it becomes coated with copper.

Silicon alloy reductant is reasonably effective for removing copper as well as zinc and trivalent chromium from an industrial effluent containing these ions, but is not reliable for reducing hexavalent chromium since the reaction is not primarily a reducing one.

SECTION II

RECOMMENDATIONS

Experiments with soft iron shot were limited to a bench scale by the scope of the project. However, results were sufficiently promising to warrent larger scale experiments, say on the order of flow rates of 1 to 2 liters per minute (16 to 32 gallons per hour).

An important advantage of larger scale experiments is the better ability to study the efficiency of copper recovery. Small scale experiments such as were carried out in this project do not generate sufficient quantities of particulate copper to collect efficiently, since much of the copper remains on the surface of the shot.

To our knowledge the kinetics of the reduction of hexavalent chromium by metallic iron have not been studied in depth. This is a potentially very useful reaction since reduction of hexavalent chromium by the usual processes is expensive and difficult to control. A detailed study such as Nadkarni et al[4,5] undertook for the cementation of copper with metallic iron and Strickland and Lawson[7] for the cementation of copper with metallic zinc would seem worth while.

Extensive study of the reaction of silicon alloys with heavy metal ions was outside the scope of this project since the reaction is not primarily a reducing one. However, the possibilities of utilizing this reaction for removal of heavy metal ions from industrial effluents is intriguing and it is recommended that such a study be carried out. It should be noted that the process has been patented.[10]

SECTION III

INTRODUCTION

GENERAL

"Cementation", i.e. the displacement of a metal from solution by a metal higher in the electromotive series, has been utilized in hydrometallurgical processes for many years.[1] Strictly speaking the term "cementation" is restricted to cases where the displaced metal is precipitated from solution, e.g. the precipitation of metallic gold by replacement with zinc supplied from zinc dust. For our purposes we are considering the term to cover reduction of any ionic species by contact with a metal of higher oxidation potential whether the reduced species is precipitated or not, i.e. the reduction of ferric ion to the ferrous form by contact with metallic iron or zinc.

Generally the application of the cementation reaction has been for the purpose of winning metals from ores or for the recovery of precious metals from scrap. In 1969, Case and Jones[2] applied the reaction to treatment of brass mill effluents to accomplish reduction of hexavalent chromium and precipitation of a significant portion of the copper. Their work demonstrated the feasibility of the application, but they did not study the reactions in depth. Further, an efficient chamber for continuous processing of feed solution which would also provide a means for separating the precipitated copper in a recoverable form was not developed. Subsequent work done at the Research and Technical Center of the Anaconda American Brass Co. resulted in the development of a rotating chamber for carrying out the reaction.[3]

While the present work is largely concerned with removing toxic elements from waste streams typical of the Brass Industry, cementation offers an attractive possibility for treating any waste stream containing reducible metallic ions which must be removed from solution. Common examples are the precipitation of silver from photographic processing solutions, the precipitation of copper from printed circuit etching solutions and the reduction of hexavalent chromium in waste streams from chromium plating, iriditing and chromate-inhibited cooling water blowdown. Zinc, aluminum and other metals having relatively high oxidation potentials may be utilized as reductants as well as iron. Alloys of certain of the alkaline earth metals, especially calcium and barium, and alloys of magnesium have also been utilized.[9, 10]

Since the reductant material is usually scrap metal which is low in cost and the process offers the possibility of recovering valuable metals such as copper and silver, the use of cementation for treating waste streams presents significant economic advantages. Case and Jones[2] compared the cost of treating the discharge from a medium-sized brass

mill by a conventional system utilizing sulfur dioxide for reduction of hexavalent chromium with the cost of treating the stream with scrap iron for precipitation of a significant portion of the copper, as well as reduction of the hexavalent chromium. Including capital costs for equipment (15-year life), operating costs and the value of the recovered copper, the cementation system showed a cost advantage of nearly $40,000 per year.

WORK BY OTHERS

A detailed study of the kinetics of copper precipitation has been carried out by Nadkarni et al[4,5] who worked with metal plates, wire and granulated cast iron suspended in a stirred solution of copper sulfate containing approximately 1 gram per liter of copper.

Experimental data were obtained by measuring the amount of copper and iron ions in solution at successive time intervals. Among the conclusions reached were:

1. Copper cementation is a first order reaction rate process. The specific rate is only slightly dependent upon initial copper concentration and pH.

2. At lower stirring speeds the rate-controlling process is solution diffusion.

3. At high stirring speeds the rate-controlling process is bulk solution diffusion through a limiting boundary film.

4. The back reaction due to ferrous ions is negligible.

5. The direct reaction of ferric ions does not normally affect kinetics of cementation as much as the reaction between ferric ions and the deposited copper.

6. Oxygen in solution causes excess iron consumption due to rapid reaction with the deposited copper, the metallic iron and ferrous ions.

7. In a nitrogen atmosphere excess iron consumption only varied slightly with pH in the pH range of 1.5 to 3.0 as long as the copper ion concentration was over 150 ppm. At lower copper ion concentrations excess iron consumption increased markedly and was roughly proportional to the hydrogen ion concentration.

Rickard and Fuerstenau[6] carried out an extensive electrochemical investigation of the cementation of copper by iron using galvanostatic electrode measurements. Solutions of copper sulfate up to approximately 0.05 M were used as electrolyte and Ferrovac E (high-purity iron), steel and cast iron as anodic materials. The authors conclude that the cementation process can be described as a galvanic corrosion cell and

present a simplified model. Other conclusions include:

1. The specific rate constant for cupric ion reduction is about twice as large as for ferric ion reduction.

2. Hydrogen ion reduction in solutions containing oxygen is dependent on the amount of oxygen dissolved in the solution. Normally the rate of hydrogen ion reduction is much slower than that of copper.

3. An increase in agitation will produce an equivalent increase in reduction rates of both ferric and cupric ions up to a limiting value.

A comprehensive study of the cementation of copper with zinc has been undertaken by Strickland and Lawson[7] who present an excellent summation of the cementation reaction mechanism. They used a rotating disc technique developed by Levich[8], using discs of the reductant metal (iron as well as zinc) immersed in a sulfate solution containing 10 ppm of copper. Conclusions include:

1. Cementation is a diffusion controlled reaction with the reaction rate being highly dependent on the presence of previously deposited copper.

2. When the specific mass of deposited copper is less than about 0.35 mg/cm^2, the absolute cementation rate per unit initial zinc area increases with:

   a. increasing reactant concentration
   b. increasing relative velocity between reactant surface and solution
   c. increasing temperature
   d. decreasing solution viscosity

3. For specific deposit masses in excess of the critical, the reaction rate is enhanced by increased roughness.

4. The deposit is sufficiently porous that, normally, the diffusion of product ions to the solution-deposit interface does not become controlling.

Recently McKavney et al[9,10] have described experimental work utilizing silicon alloys for removal of heavy metals from water and brine. It was at first thought that this reaction involved metal "exchange" and was, therefore, analagous to cementation, however, our own work showed the primary mechanism to be otherwise. This work will be further discussed in the body of the report.

Hoover and Masselli[11] proposed the use of scrap iron for the reduction of hexavalent chromium in waste liquors from chromium plating in 1941. Since that time the only published work discussing this reaction we

have found is that of Case and Jones.[2]

PURPOSE OF PRESENT WORK

Most previous investigations of the cementation reaction have been oriented toward a hydrometallurgical application. The present work differs in that it is oriented toward an industrial waste, anti-pollution, application. This difference is important in at least two fundamental respects:

1. The concentration of reducible ions in industrial waste streams is much lower than in most metallurgical process streams and the lower concentrations are more difficult to reduce efficiently.

2. The metal ion concentrations in the waste ultimately discharged must be extremely low, usually 1 ppm, or less, thus necessitating very efficient separations.

Because of the orientation of this work we tried to use experimental systems which might be scaled directly to an industrial application.

THEORY OF CEMENTATION

Strickland and Lawson[7] have expounded the theory of cementation in considerable detail. As explained previously in this work we are concerned with the reduction of any ionic species by contact with a metal of higher oxidation potential. In particular we worked principally with the copper-iron and the hexavalent chromium-iron systems.

Copper-iron system

The copper-iron system differs from some similar systems because of the side reactions involving oxygen. The reactions are as follows:

$$CuSO_4 + Fe \rightarrow FeSO_4 + Cu \quad (1)$$

$$H_2SO_4 + Fe \rightarrow FeSO_4 + H_2 \quad (2)$$

$$4FeSO_4 + 2H_2SO_4 + O_2 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O \quad (3)$$

$$2Cu + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O \quad (4)$$

$$2Fe + 2H_2SO_4 + O_2 \rightarrow 2FeSO_4 + 2H_2O \quad (5)$$

$$Fe_2(SO_4)_3 + Fe \rightarrow 3FeSO_4 \quad (6)$$

$$Fe_2(SO_4)_3 + Cu \rightarrow CuSO_4 + 2FeSO_4 \quad (7)$$

$$Fe_2(SO_4)_3 + 6H_2O \rightleftarrows 2Fe(OH)_3 + 3H_2SO_4 \quad (8)$$

Equation (1) is the basic cementation reaction which it is desired to complete. It will be seen that the reaction does not consume acid and is thus not pH dependent (except, as will be explained later, pH values above approximately 3.5 lead to precipitation of hydrous oxides and basic salts of iron and copper). It is also apparent that for the precipitation of one unit of copper, theoretically 0.8789 units of iron are required.

All of the other reactions are competing side-reactions which it is desirable to suppress. Nadkarni and Wadsworth[5] have discussed the kinetics of all these reactions in considerable depth.

Equation (2) defines the dissolution of iron with acid. It proceeds more slowly than (1) but cannot be completely suppressed. In our work it is the reaction which we tried to minimize.

Equations (3), (4), and (5) show the influence of oxygen on the reduction system. It is obvious that oxidation of any of the components of the system will increase the iron consumption by providing reducible ionic species. The effects of oxygen on the system can be eliminated by carrying out the reaction in a reducing or an inert atmosphere. It is of especial advantage to carry out the cementation reaction under hydrogen, which in any event is generated according to equation (2), since the hydrogen itself has some reducing action on the cupric ion. Back[12] has described a commercial system which takes advantage of this fact.

Equations (6) and (7) define the reactions between ferric salts and metallic iron and copper respectively. Obviously this reaction can be prevented by eliminating oxygen from the system (unless ferric ion is already present in the feed solution, as is usually the case in leach liquors).

Equation (8) illustrates the precipitation of ferric hydroxide by hydrolysis which occurs between pH 3 to 4. This is undesirable since the ferric hydroxide coats the surface of the metallic iron and also may induce coprecipitation of basic copper sulfate.

Hexavalent chromium - iron system

As previously mentioned, not much work on this system has appeared in the literature. The reactions are:

$$Na_2Cr_2O_7 + 7H_2SO_4 + 2Fe \rightarrow Na_2SO_4 + Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + 7H_2O \quad (9)$$

$$Na_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \rightarrow Na_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O \quad (10)$$

Equation (9) is the basic reaction. It will be noted that the reaction requires acid and is thus pH dependent, that the iron is oxidized to the ferric state and that for each unit of hexavalent chromium reduced, 1.0741 units of iron are required.

In the presence of ferrous ion (such as would result from cementation of copper in the same solution) the reaction defined by (10) takes place.

Under the proper conditions of pH, diffusion, and ratio of iron surface to reducible ion the reaction is quantitative and extremely rapid.

The following reaction is also possible in the presence of cemented copper:

$$Na_2Cr_2O_7 + 7H_2SO_4 + 3Cu \rightarrow Na_2SO_4 + Cr_2(SO_4)_3 + 3CuSO_4 + 7H_2O \qquad (11)$$

However, reactions (9) and (10) are so rapid it is doubtful that there is ever sufficient residual hexavalent chromium present for reaction (11) to proceed.

In a solution of pH 2.0 or less containing both copper and hexavalent chromium in the absence of air the probable sequence of reactions is: (9), (1), (2), (6), (7).

SECTION IV

USE OF IRON SHOT AS REDUCTANT

Small diameter shot appeared to us to have several advantages from the standpoint of geometry, including:

1. Relatively large surface area per unit volume.

2. Point-to-point contact between pieces rather than surface-to-surface contact.

3. Good mixing action.

4. Easily controlled surface area.

REDUCTANT

The shot utilized was obtained from Crossman Arms Co. Inc., Freeport, N.Y.. Analysis showed it to have a carbon content of approximately 0.05% and only traces of metallic contaminants. The shot had an average diameter of 4.37 mm, an average weight of 0.34 grams and a packing density of 642 shot per 50 ml. Thus 50 ml of shot had a surface area of approximately 385 cm^2. The shot as received was covered with a film of lubricant which was removed by a hot water and soap solution followed by an acetone rinse. Normally the shot was cleaned by pickling in a mixture of 25% NH_4OH (sp. gr. 0.90) plus 5% H_2O_2 (30%) immediately before use and between runs.

When a volume of less than 50 cc of shot was used in order to reduce the iron surface, the difference in volume was made up by adding chemically-resistant glass beads of approximately the same diameter. It was thought that this would keep the shear rate between the solids and the solution relatively constant.

REACTOR

The reactor was a 500-ml Erlenmeyer flask mounted about 30° from the horizontal on a circular plate capable of revolving at speeds up to 60 RPM. In most experiments nitrogen was fed through a tube reaching nearly to the bottom of the flask at the rate of 2 liters per min.

When the reactor was operated on a continuous basis the feed solution was pumped into the flask through a tube reaching nearly to the bottom and the overflow allowed to drip off a collar around the mouth of the flask into a collection beaker. Fig. 1, shows the arrangement.

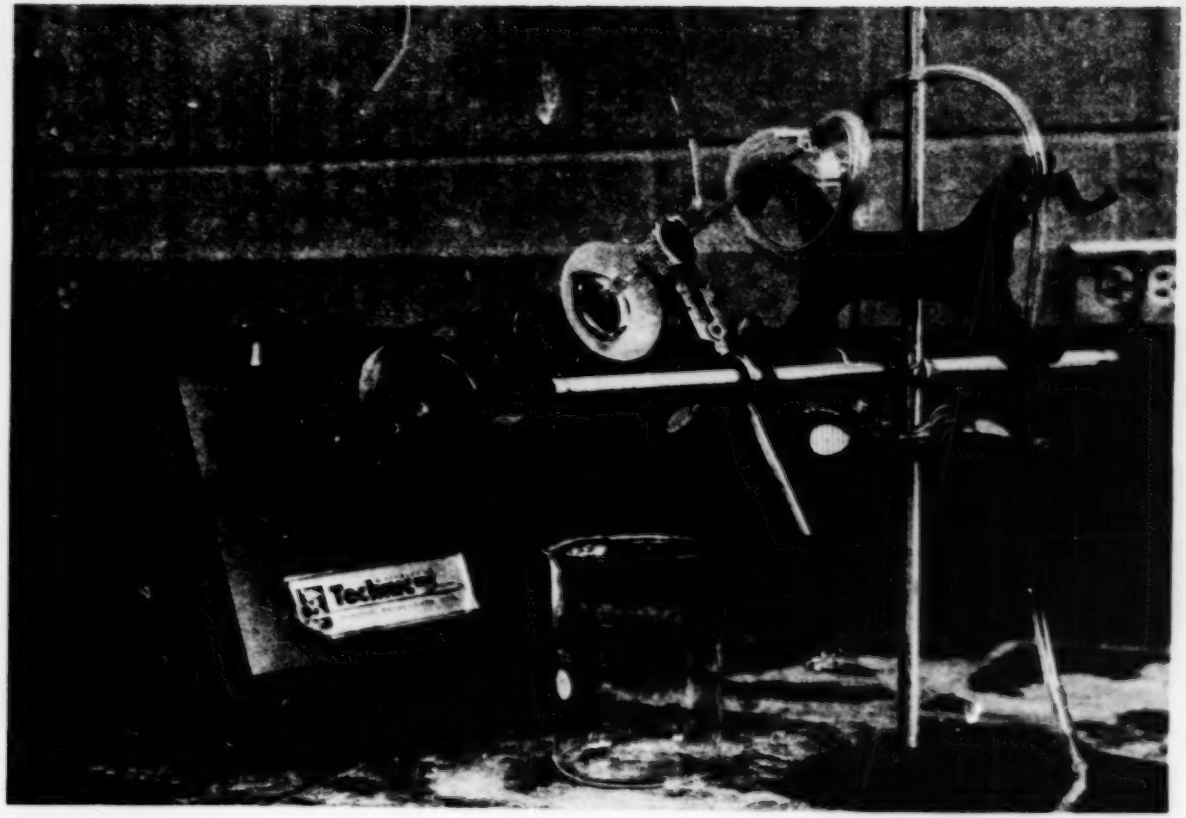

Figure 1. Reactor Utilized for Reduction Experiments with Iron Shot

FEED SOLUTIONS

Feed solutions were normally made up to contain 100 ppm of the reducible ion species (copper and hexavalent chromium) which is the highest level likely to be found in brass mill discharges. Reagent grade $CuSO_4.5H_2O$ was used as a source of cupric ion and $Na_2Cr_2O_7.2H_2O$ of similar purity was used as a source of hexavalent chromium ion. The pH of the solutions was adjusted with H_2SO_4 or NaOH.

EXPERIMENTAL PROCEDURES

Experiments were carried out by both batch and continuous reactions. The procedures will be formed in Appendix A, page 33.

EXPERIMENTAL RESULTS (BATCH REACTIONS)

Copper only in feed solution

Effect of pH- The pH of feed solutions was adjusted to 1.50, 1.90, and 3.00 and the solutions reacted with 50 cc of shot in air. Curves illustrating the results are plotted on Fig. 2.

It will be noted that in all instances 99% of the copper was removed in 10 min . The rates of removal were quite similar, although the rate appeared to be slightly higher at pH 3.0. However, since the initial pH of the solution quickly rose to nearly 5, ferric iron precipitated as ferric hydroxide and probably carried some copper in the form of basic sulfate with it. The fact that the precipitates from runs at pH 1.5 and 1.9 carried a negligible amount of copper, whereas precitates from runs at pH 3.00 averaged nearly 1 mg of copper lends credence to this probability. Hence, there is probably no real difference in the rates of the reaction.

The fact that a higher level of excess iron dissolved in a solution having an initial pH of 1.90 than in one having an initial pH of 1.5 is puzzling. A possible explanation may be the increased oxidation of ferrous ion at higher pH. Data for excess iron dissolved in a solution having an initial pH of 3.00 is not available. As previously mentioned, a significant part of the dissolved iron precipitated as ferric hydroxide.

Only at the median initial pH was the rise in pH gradual. At both higher and lower acid concentrations the pH leveled out rapidly. At the higher pH this results from the equilibrium by the precipitation of ferric hydroxide. At the lower pH it results from the fact that relatively large changes in hydrogen ion concentration result in only small pH changes in this area. It is interesting to note that at the median initial pH the curves for pH rise and excess iron dissolution roughly parallel each other.

Effect of oxygen- To assess the effect of eliminating oxygen from the

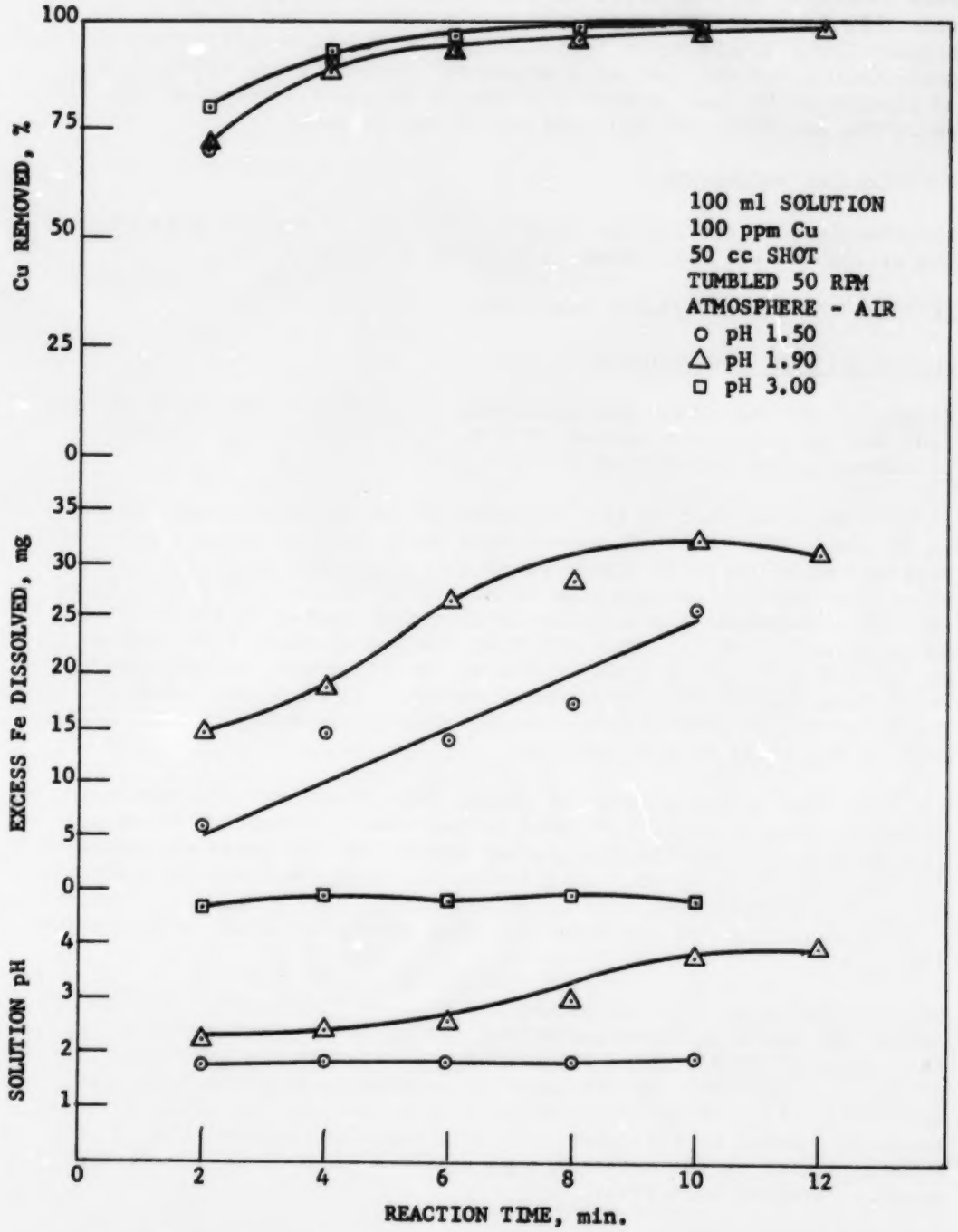

Figure 2. Effect of pH of Feed Solution on Copper Cementation with Iron Shot

system, nitrogen was bubbled through solutions at 2 liters/min. during a series of runs. Also included in this series of experiments were runs made without any copper in the feed solution. Curves illustrating the results are plotted on Fig. 3.

The rate of copper removal was better in the nitrogen atmosphere. This may be due to the fact that re-solution of copper by oxidation was prevented.

Interestingly the level of excess dissolved iron remained fairly constant in the nitrogen atmosphere. This seems to confirm the observations of Nadkarni and Wadsworth[5] on the increased iron consumption resulting from oxidation. It is however, surprising to note that iron dissolution is at a lower level when there is no copper present in solution; quite possibly the metallic copper deposited on the surface of the iron catalyzes the dissolution.

In the absence of copper the pH levels out at a slightly higher value. This is at variance with the fact that slightly less iron is dissolved under the same conditions.

Effect of surface area- Runs were made using 50 cc, 25 cc, and 12.5 cc of shot. Where less than 50 cc of shot was used the volume was made up to 50 cc with glass beads. Data illustrating the results are shown on Fig. 4.

It is evident that the efficiency of the reaction is not directly proportional to the surface area of the iron. For instance, by reducing the surface of the iron from 385 cm^2 to 193 cm^2, the amount of copper removed from the solution in 10 min. is reduced only 8%, although the excess iron dissolved is halved and the pH rise is reduced by more than 90%.

By reducing the surface of the iron from 385 cm^2 to 96 cm^2, the amount of copper removed from the solution in 10 minutes is reduced only 36%, whereas the excess iron dissolved is only about one fifth and the pH rise is reduced by about 95%.

It seems obvious that in practice it is advantageous to use the minimum iron surface which will accomplish satisfactory copper removal in a reasonable time. From the data shown on Fig. 4, at the 100 ppm copper level a minimum of about 200 cm^2 of iron surface is required to remove 90% of the copper from 100 ml of solution during a contact period of 10 min. (equivalent to approximately 0.045 mg Cu/cm^2Fe). During this period about 13 mg of excess iron will be dissolved (equivalent to approximately 1.4 mg excess Fe/mg Cu cemented).

Effect of previously deposited copper- To determine the effect of previously deposited copper on the efficiency of the iron reductant six consecutive 10-min. runs were made using the same charge of shot.

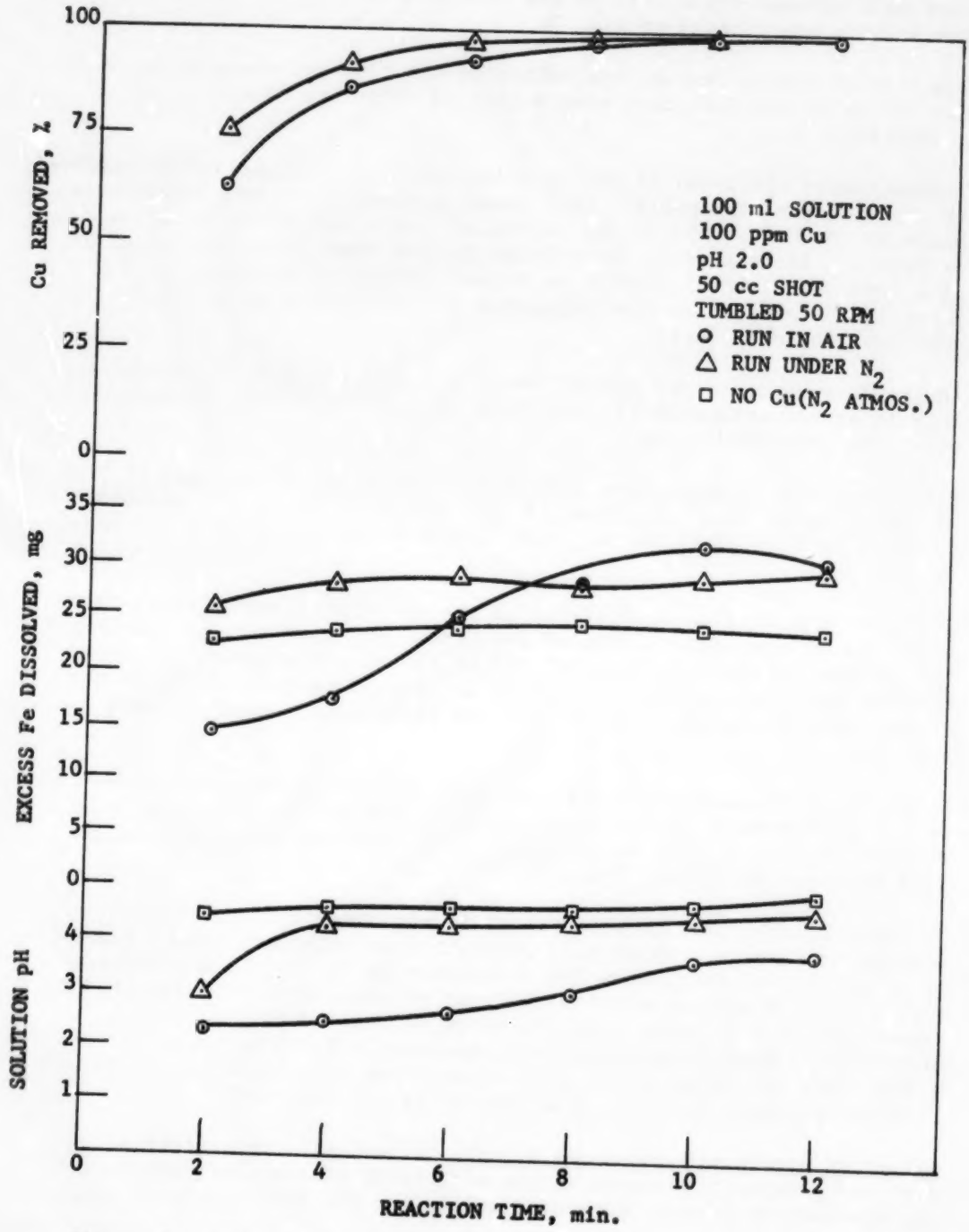

Figure 3. Effect of Oxygen on Copper Cementation With Iron Shot

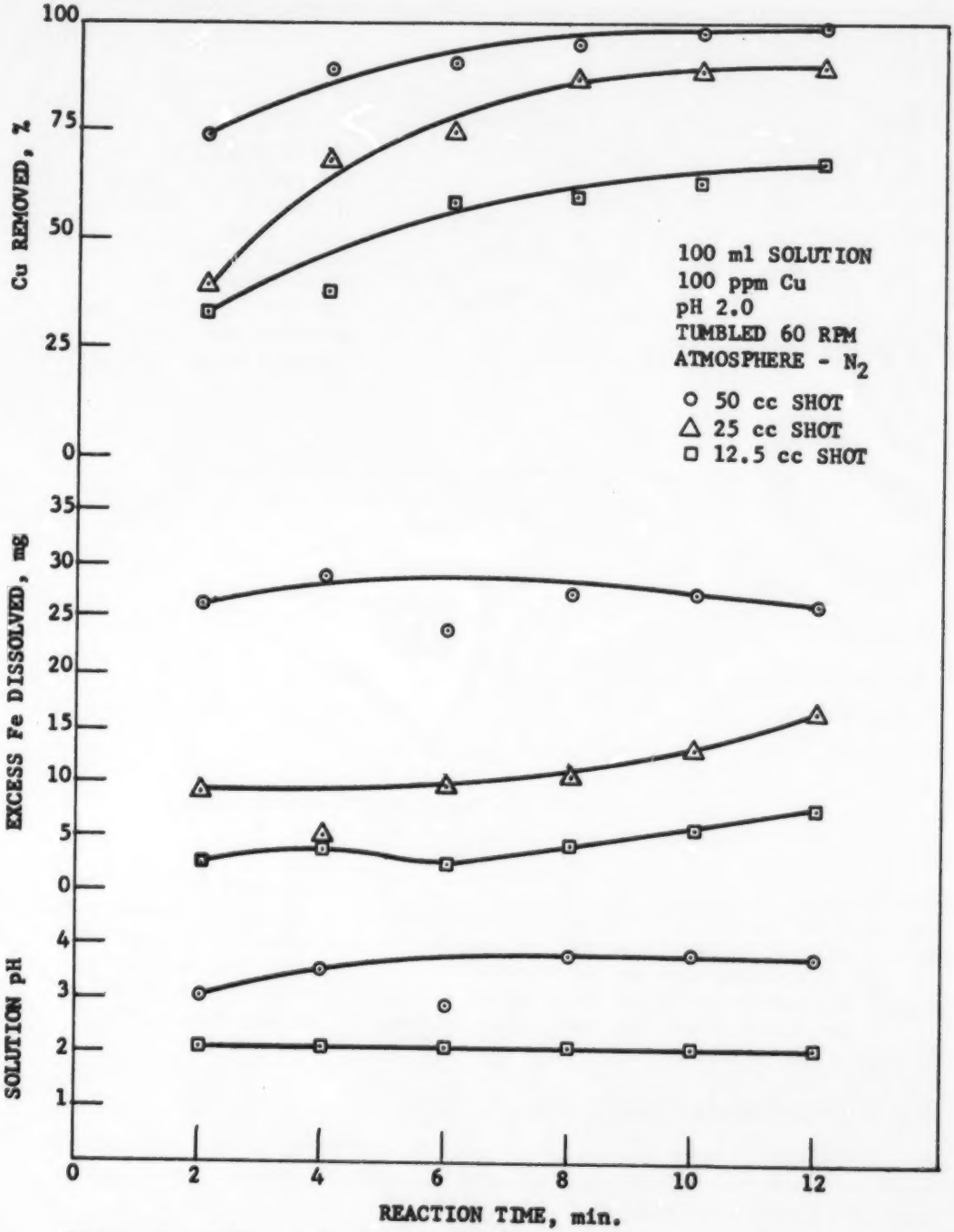

Figure 4. Effect of Surface Area of Reductant on Copper Cementation With Iron Shot

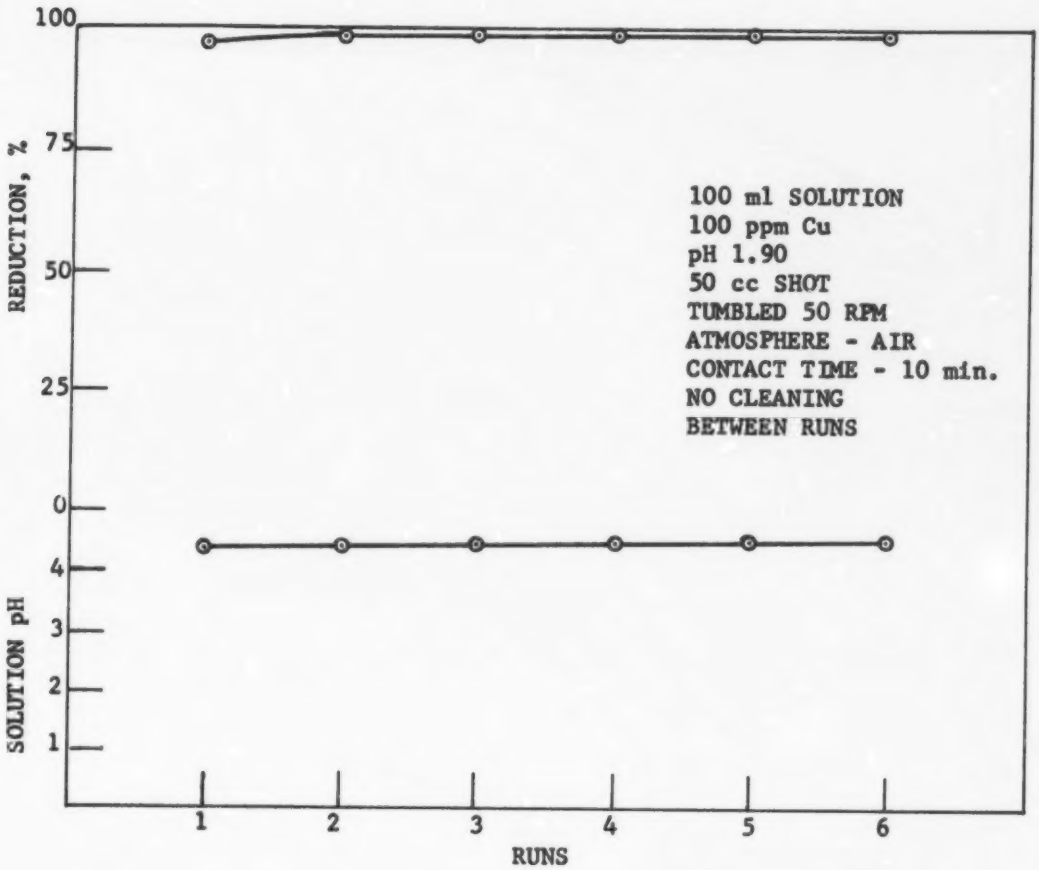

Figure 5. Effect of Previously Deposited Copper on Copper Cementation With Iron Shot

Results are plotted on Fig. 5. Since the runs were made in air substantial amounts of ferric ion were precipitated as hydroxide. The data show that better than 99% of the copper was removed during each run and that there was no deterioration of efficiency in succeeding runs. Evidently any film which forms on the surface of the iron is porous enough so that the feed solution readily penetrates to the metal. This confirms the observation of Strickland and Lawson[7].

Hexavalent chromium only in feed solution

In experimenting with hexavalent chromium solutions it quickly became apparent that the reduction proceeded rapidly to completion. Typical data are plotted on Fig. 6.

When these data are compared with those for copper under the same

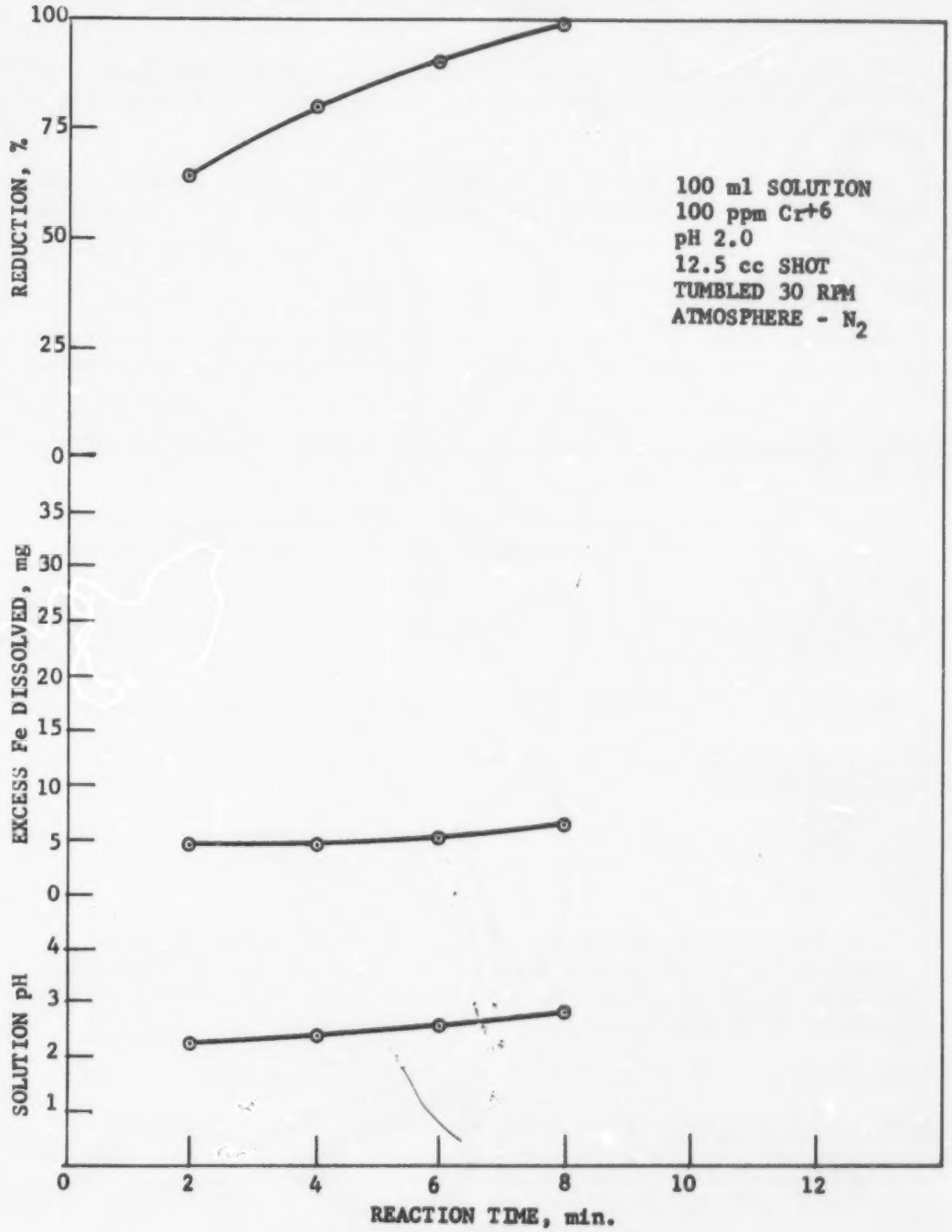

Figure 6. Reduction of Hexavalent Chromium With Iron Shot

conditions which are plotted on Fig. 4 it is apparent that:

1. The chromium reduction is complete in 8 min. whereas the copper removal is only about 60% complete in 8 min. and never reaches much above 70% completion.

2. The chromium reduction results in dissolution of slightly more excess iron than the copper cementation, probably due to presence of ferric ion.

3. The pH rise during the chromium reduction is a little greater than that which occurs during copper cementation. This is to be expected since the reaction consumes acid.

Copper and hexavalent chromium in feed solution

Experiments were run to study the effect of equal amounts of copper and hexavalent chromium upon the reduction of each other. Data are plotted on Fig. 7.

Effect of hexavalent chromium on copper cementation- Examination of the data shows:

1. The presence of hexavalent chromium suppresses the copper cementation. For a contact time of 8 min. the cementation of copper is about 16% less.

2. The presence of hexavalent chromium also suppresses the dissolution of excess iron.

3. The presence of hexavalent chromium causes an increase in pH rise.

Effect of copper on the reduction of hexavalent chromium- The following effects are apparent:

1. The presence of copper increases the rate of reduction of hexavalent chromium slightly. This effect was also noted by Hoover and Masselli[10].

2. The copper suppresses the dissolution of excess iron. This is contrary to the effect noted during a continuous run where, as will be seen later, the dissolution of excess iron was increased in the presence of copper.

3. The copper has little effect on the pH rise during the reaction.

Effect of mixing speed- Since reduction by a solid material is a diffusion controlled reaction, the speed of mixing necessarily influences the rate of reduction. Data obtained by increasing the tumbling rate from 30 to 60 RPM are plotted on Fig. 8. It will be noted that a slight increase in the copper cementation rate occurred. Reduction of

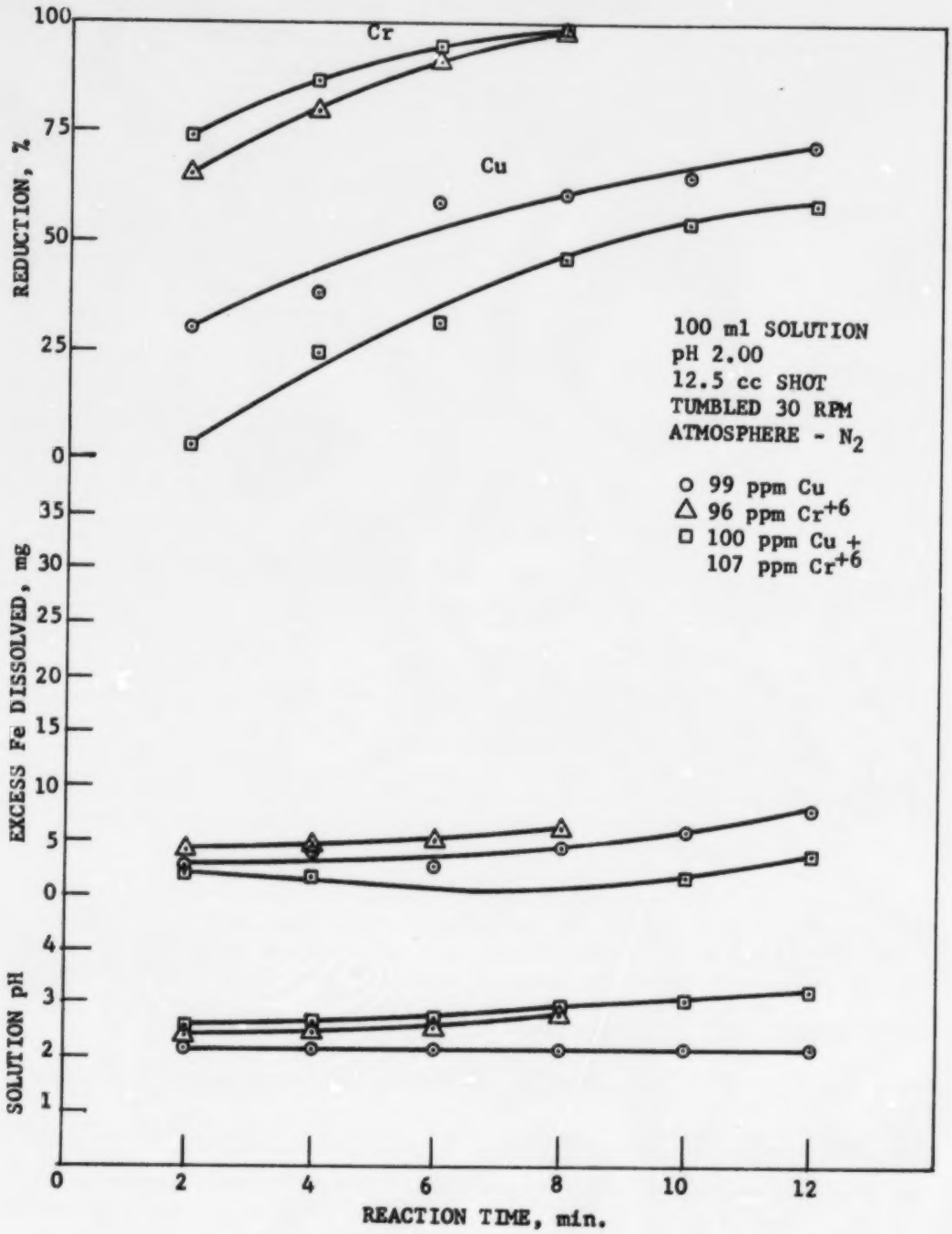

Figure 7. Simultaneous Cementation of Copper and Reduction of Hexavalent Chromium With Iron Shot

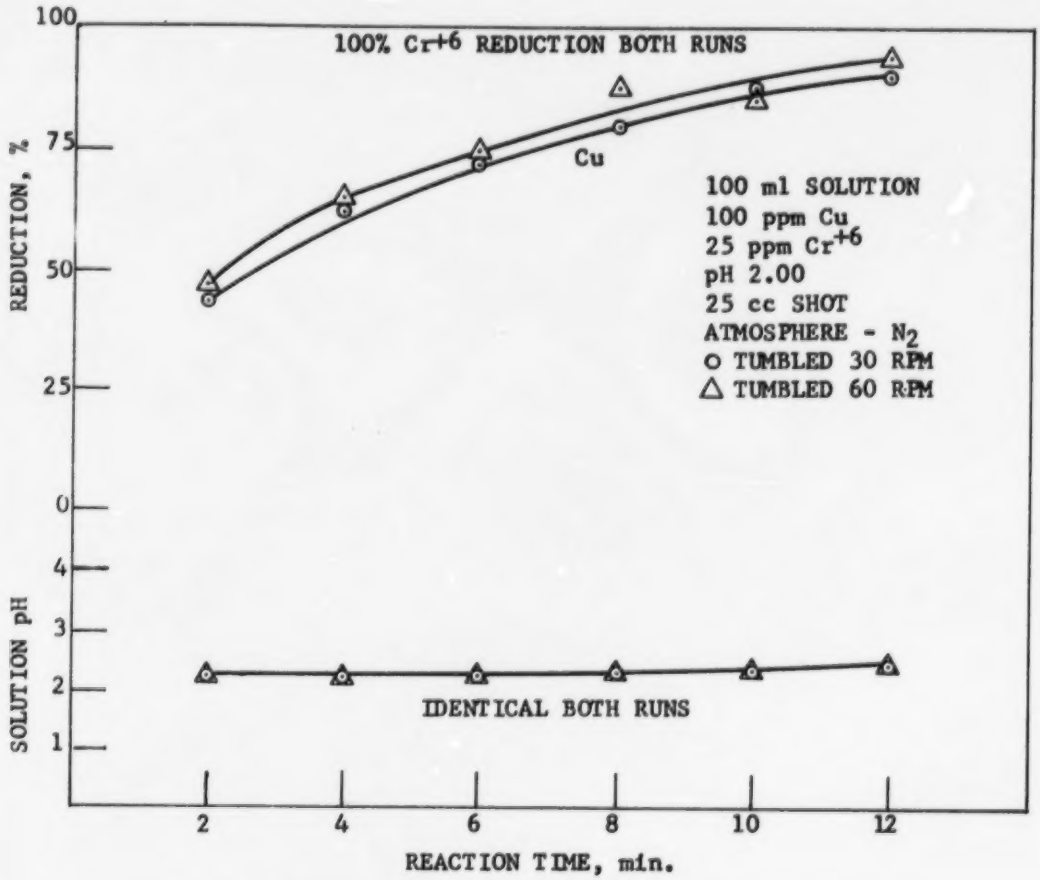

Figure 8. Effect of Speed of Mixing on Simultaneous Copper Cementation and Reduction of Hexavalent Chromium With Iron Shot

hexavalent chromium was almost instantaneous in both instances. There was no effect on pH rise. It is probable that the results would have been more pronounced if the change in rotational speed had been greater or the ratio of iron shot volume to liquid volume had been greater.

EXPERIMENTAL RESULTS (CONTINUOUS REACTIONS)

Data are plotted on Fig. 9. The following conclusions may be drawn:

Copper only in feed solution

1. The rate of copper cementation stabilized quite rapidly and did not change greatly during the course of the experiment. The amount of copper cemented averaged a little over 79%.

2. The amount of excess iron dissolved increased very gradually and finally stabilized at about 320 ppm.

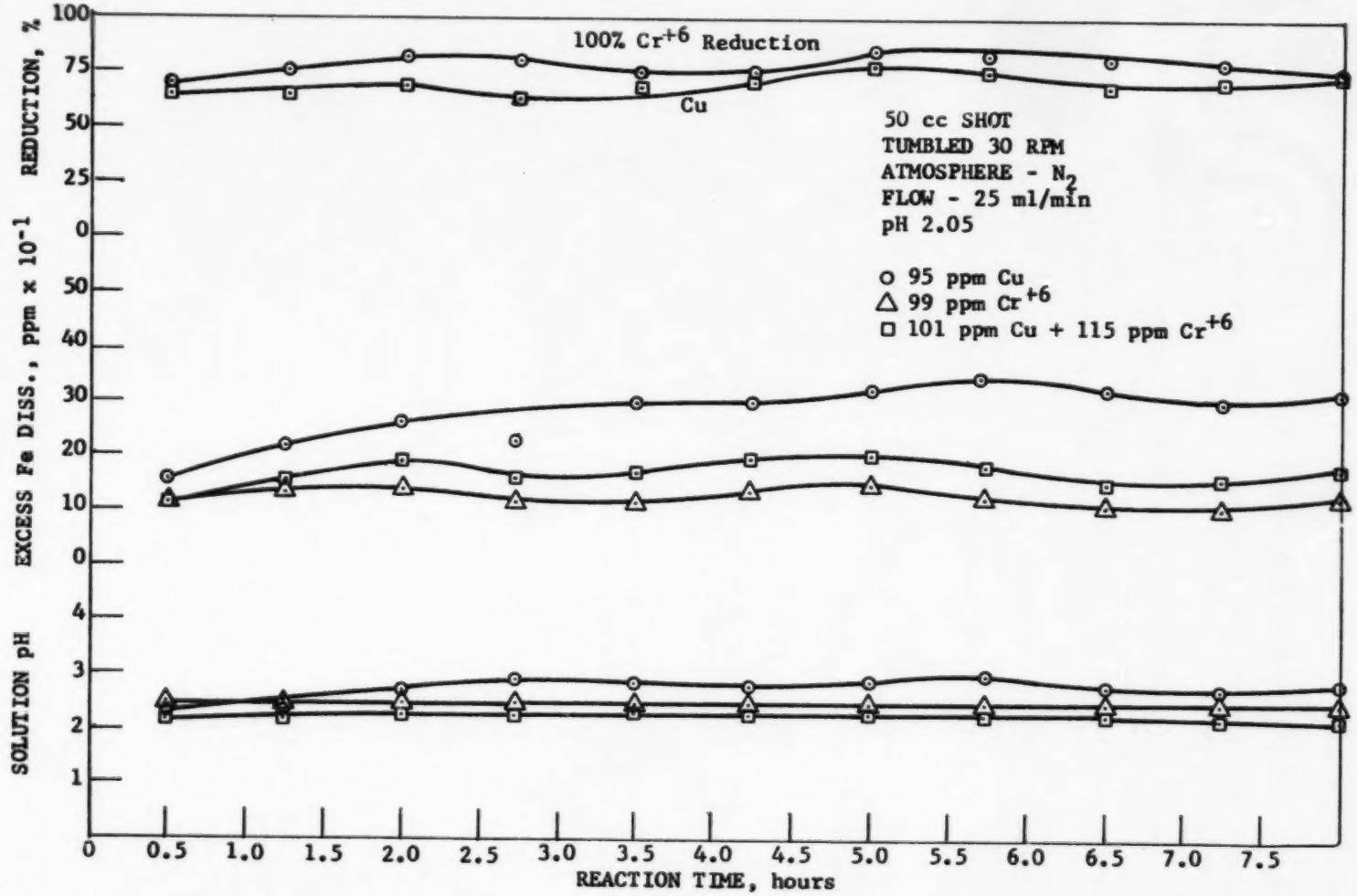

Figure 9. Continuous Cementation of Copper and Reduction of Hexavalent Chromium With Iron Shot

3. The pH also increased very gradually and stabilized at about 2.75. It is interesting to note that the curves for excess iron dissolution and the pH rise closely parallel each other.

Hexavalent chromium only in feed solution

1. Hexavalent chromium was quantitatively reduced almost immediately and continued to be so during the course of the experiment.

2. The amount of excess iron dissolved stabilized fairly quickly at about 129 ppm; less than 20% of the amount dissolved by the copper cementation under the same conditions. It is interesting to note that even though the system contained a substantial excess of iron surface (in terms of the requirements for quantitative reduction of the hexavalent chromium) the amount of excess iron dissolved was very low. This may indicate that under stabilized dynamic conditions the presence of chromium inhibits dissolution of iron by acid.

3. The pH remained constant at about 2.55, slightly lower than for the copper cementation, probably because less acid was expended in the dissolution of iron.

Copper and hexavalent chromium in feed solution

1. Again the reduction of hexavalent chromium was quantitative during the course of the experiment. However, the cementation of copper was slightly depressed, averaging only 71.29%.

2. The dissolution of excess iron was considerably less than when copper alone was present in the solution, but slightly greater than when chromium alone was present. It is significant that the curves for excess iron dissolution by chromium alone and by chromium plus copper parallel each other closely, indicating the dominating effect of the chromium.

3. The pH remained constant at a very slightly lower level than where chromium alone was present in the feed solution.

Not apparent from the data is the observed fact that during the continuous runs fairly large particles of copper were continually dislodged from the surface of the shot. While some of these were swept out of the reactor by the flow of solution, most collected in the bottom of the reactor. It seems likely that at higher flow rates coupled with a lesser angle of inclination of the reactor most of the precipitated copper would eventually be swept from the reactor and could be settled in a collection chamber. During batch runs where only 10 mg of copper was present, 90% or more of the copper adhered to the surface of the shot.

SECTION V

USE OF PARTICULATE IRON AS REDUCTANT

Back[12] has described the advantages of particulate iron as a medium for the commercial cementation of copper. This material was explored only briefly in the present work because the use of iron shot seemed much more suitable for a small-scale laboratory system.

REDUCTANT

Two different sizes of iron particles were used: approximately -400 mesh (Leco Low-Sulphur Iron Powder Accelerator No. 501-78, Laboratory Equipment Corp., St. Joseph, Mich.) and -325 mesh (ACF Powder, Hoeganaes Corp., Riverton, N.J.).

FEED SOLUTION

The feed solution contained 100 ppm of Cu as $CuSO_4$ and had a pH of 2.0.

EXPERIMENTAL PROCEDURES

The system was tested only with copper and only in batch reactions. The procedures will be found in Appendix B, page 34.

EXPERIMENTAL RESULTS

It was observed that initially iron powder of either type was uniformly dispersed throughout the feed solution, however, as copper was cemented on the surface the individual particles began to clump together until finally most of the metal remained on the bottom of the reaction vessel. Data for both runs are plotted on Fig. 10. The data for the two runs are not directly comparable with each other or with any of the data obtained with iron shot.

Several facts may be observed from the data:

1. The removal of copper in the mechanically stirred system gradually deteriorated with time. This is no doubt due to the "clumping" of the iron particles.

2. The removal of copper in the nitrogen-dispersed system gradually increased with time, probably because the "clumping" effect was not as serious when a fresh charge of iron was used for each run.

3. The amount of excess iron dissolved in the mechanically stirred system gradually decreased after an initial sharp drop, whereas the

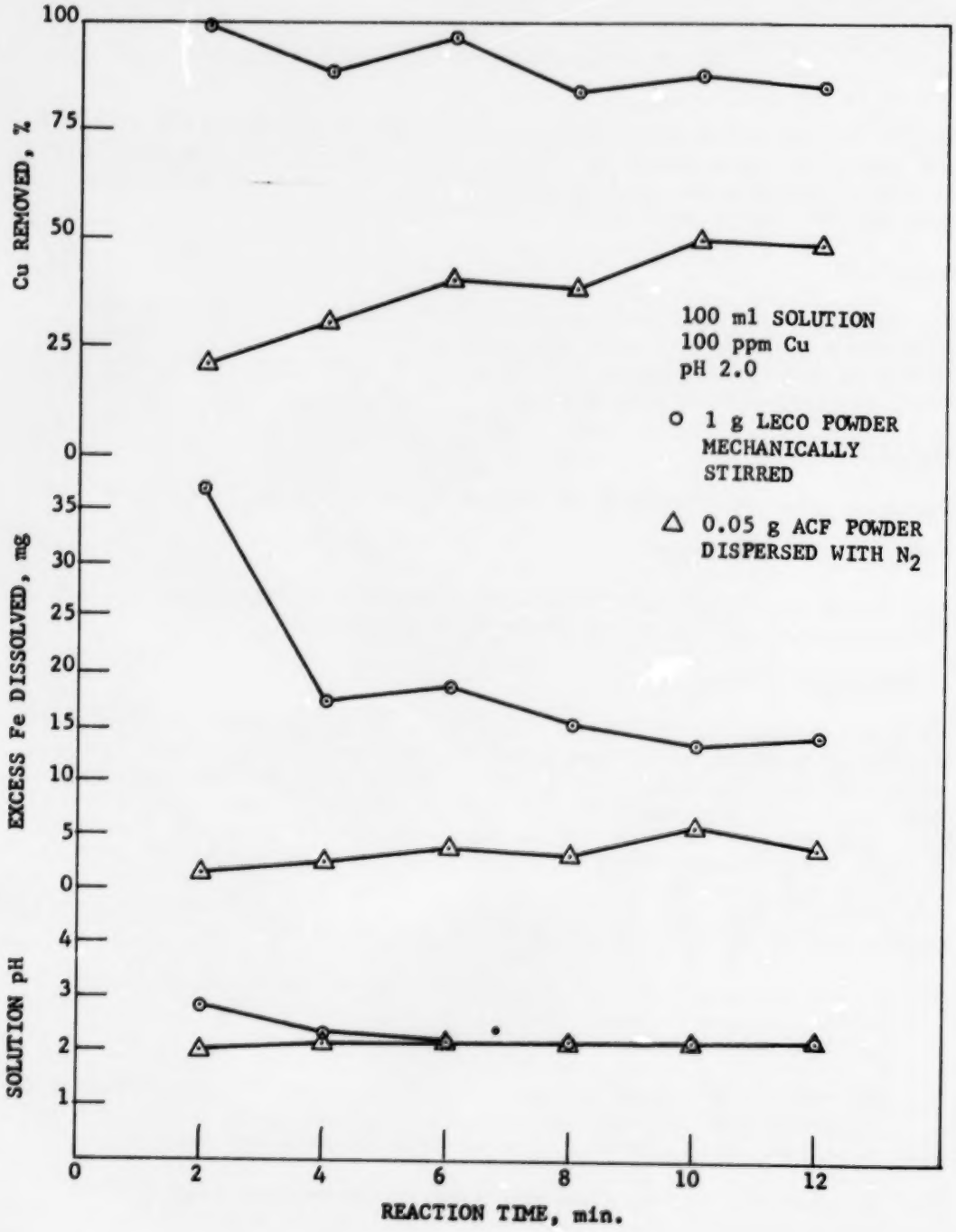

Figure 10. Cementation of Copper With Particulate Iron

amount very gradually increased in the nitrogen-dispersed system; probably for the same reason as the variation in the behavior of the copper cementation.

4. There was little rise in pH with increase in contact time in either system.

We believe the tendency of the cemented copper to adhere to the iron particles and the resulting "clumping" of the particles greatly limits the usefulness of this medium. Possibly these effects can be overcome by using a high flow rate to keep particles in suspension.

SECTION VI

USE OF SILICON ALLOYS AS REDUCTANT

BACKGROUND

As previously noted, McKavney, Fassinger and Stivers[9] have described a system which utilizes silicon alloys (especially alloys with calcium and magnesium) for the removal of heavy metals, including copper, zinc and chromium, in concentrations of 5 to 100 ppm from waste water. They carried out batch reactions by shaking a solution containing heavy metal ions with the granulated silicon alloy in a flask and semi-continuous reactions by passing the solution containing the heavy metals through a 150 mm x 30 mm I.D. column packed with the alloys.

Removal of copper, zinc, trivalent chromium and other heavy metals was impressive, however the reduction (and removal) of hexavalent chromium was not satisfactory. The advantage over conventional removal techniques claimed for the process is the fact that the only ion going into solution is calcium or magnesium, neither of which is generally considered objectionable in a waste stream. The authors explained the mechanism of reaction as being primarily electrochemical with possible hydroxide formation through hydrolysis.

Because of the presumed analogy to the "cementation" reaction we investigated the sytem both on a batch and a continuous (plug-flow reactor) basis.

REACTANTS

The silicon alloys used were:

1. Magnesium Ferrosilicon (Si 44.50%, Mg 8.90%, Ca 1.00%, Fe 43.00%) supplied by Globe Metallurgical Div. of Interlake, Inc., Beverly, Ohio which was sieved to 10/20 mesh before use.

2. Calcium Silicon (Ca 32.4%, Si 63.1%, Fe 4.0%, Ba 0.4%) supplied by Union Carbide, Ferro Alloys Div., Marietta, Ohio, which was sieved to 28/65 mesh before use.

FEED SOLUTION

The feed solution used was typical of a brass mill effluent. The composition was:

Copper	45 ppm
Zinc	43 ppm
Chromium (+3)	43 ppm
Chromium (+6)	7.5 ppm
pH	2.05 ppm

All cations were present as sulfates.

EXPERIMENTAL PROCEDURES

Contact between feed solution and reactants was achieved by:

1. Magnetic Stirring (Mg-Si alloy only).

2. Tumbling.

3. Continuous flow through a vertical column.

The procedures are described in Appendix C page 35.

EXPERIMENTAL RESULTS

Magnetic Stirring

Results are shown in Table 1.

Table 1. METAL REMOVAL BY Mg-Si ALLOY REACTED BY MAGNETIC STIRRING

Run	ppm Copper Eff.	%Rem.	ppm Zinc Eff.	%Rem.	ppm Chromium^{T} Eff.	%Rem.	ppm Chromium^{+6} Eff.	%Rem.	ppm Mg Eff.	pH Eff.
1	<.5	98.9+	<.1	98.8+	<1.0	98+	0	100	160	10
2	<.5	98.9+	<.1	98.8+	<1.0	98+	0	100	190	10
3	<.5	98.9+	0.2	99.5	<1.0	98+	<.1	98.7+	200	9.8
4	0.6	98.7	0.6	98.6	<1.0	98+	0	100	202	9.8
5	0.5	98.9	0.5	98.8	<1.0	98+	0	100	204	9.85
6	0.9	98	1.1	97.4	1.2	97.6	0	100	202	9.75

Some readily apparent conclusions are:

1. In 6 successive 5-min. runs, removal of all heavy metals exceeded 97%, although there was a very slight deterioration after the 5th run.

2. The pH of the solution rapidly stabilized at 10 which approaches that of a saturated magnesium hydroxide solution.

3. After the first run the amount of magnesium which entered the solution remained fairly constant at about 200 ppm which is much higher than would be expected for a saturated magnesium hydroxide solution, indicating that some of the magnesium was present as sulfate.

A run made with 100 ml of distilled water under the same conditions as the runs with feed solution containing metal ions and acid resulted in a pH of 10.5 and a magnesium concentration of 10 ppm.

Tumbling

Mg-Si alloy- Results are shown in Table 2.

Table 2. METAL REMOVAL BY Mg-Si ALLOY REACTED BY TUMBLING

Run	ppm Copper Eff.	%Rem.	ppm Zinc Eff.	%Rem.	ppm Chromium^{T} Eff.	%Rem.	ppm Chromium^{+6} Eff.	%Rem.	ppm Mg Eff.	pH Eff.
1	<.5	99	<.1	100	6.8	87	5.0	33	80	10.25
2	<.5	99	<.1	100	8.8	83	5.0	33	60	10.25
3	0.8	98	0.2	100	8.8	83	5.5	27	57	10.2
4	<.5	99	<.1	100	6.8	87	5.0	33	49	10.1
5	<.5	99	<.1	100	5.7	89	4.0	47	40	10.0
6	3.3	93	3.0	93	12.6	75	5.0	33	54	10.0

It is evident that:

1. Removal of copper and zinc is satisfactory for the first 5 runs, but efficiency drops off after the 5th run.

2. Removal of trivalent chromium is fairly satisfactory, though less complete than for copper and zinc.

3. Removal of hexavalent chromium is unsatisfactory.

4. The amount of magnesium taken into solution is only about one-third the amount dissolved by the more vigorously stirred solutions.

5. There is a marked deterioration in efficiency of removal of all metals after the 5th run. The reason for this is not clear since the pH remained constant at about 10.

The precipitates from runs 4 and 5 were analyzed for copper, zinc, and chromium. Results are tabulated in Table 3.

Table 3. PRECIPITATED METALS RECOVERED AFTER REACTION OF FEED SOLUTION WITH Mg-Si ALLOY

Run	mg Copper Rem.	Rec.	%Rec.	mg Zinc Rem.	Rec.	%Rec.	mg Chromium Rem.	Rec.	%Rec.
4	4.5	4.0	89	4.3	2.8	65	4.4	3.3	75
5	4.5	3.2	71	4.3	2.4	56	4.5	2.7	60

We believe the results to indicate that a significant amount of the precipitated metals remains on the surface of the reactant metal.

Ca-Si Alloy- Results are shown in Table 4.

Table 4. METAL REMOVAL BY Ca-Si ALLOY REACTED BY TUMBLING

Run	ppm Copper Eff.	%Rem.	ppm Zinc Eff.	%Rem.	ppm Chromium^{T} Eff.	%Rem.	ppm Chromium^{+6} Eff.	%Rem.	ppm Ca Eff.	pH Eff.
1	<.5	99	0.2	99+	2.0	96	1.2	84	100	9.95
2	<.5	99	<.1	100	1.8	96	1.2	84	96	9.35
3	<.5	99	0.5	99	1.3	97	1.0	87	84	7.95
4	1.1	98	0.8	98	3.4	93	1.4	81	100	7.95
5	1.1	98	8.7	80	2.4	95	1.0	87	74	6.35
6	7.2	84	39	9	12.6	75	1.2	84	48	5.05

Significant differences from the behavior of the magnesium-silicon alloy include:

1. Removal of zinc decreases rapidly after the 4th run, probably because of the drop in pH.

2. Reduction of hexavalent chromium remains fairly constant at 85% through the first 5 runs. This is significantly better than achieved with the magnesium alloy, probably because of the higher oxidation potential of calcium.

3. The pH drops progressively as runs are continued.

4. The amount of calcium dissolved drops progressively as runs are continued. This may be because all of the calcium has been leached from the surface of the alloy or because the surface has been coated with a film of reaction products which inhibit further dissolution.

Continuous (Plug-Flow) Reaction

Results are shown in Table 5.

Table 5. METAL REMOVAL BY Mg-Si ALLOY REACTED BY CONTINUOUS FLOW

Elapsed Time, Min.	Zn %Rem.	Cr %Rem.	Fe %Rem.	Fe in effluent	Mg in effluent	Si in effluent	pH
				*	*	*	
0-15	98	99	86	<.5	58	5	9.70
15-30	92	91	78	<.5	61	6	10.10
30-45	91	89	74	<.5	62	6	10.05
45-60	88	86	71	<.5	60	6	10.0
60-75	82	78	65	<.5	63	7	10.0
75-90	80	77	63	<.5	65	7	9.95

*ppm

It will be noted that all of the metals were removed less effectively with the passage of time.

During the course of the run it was noted that the effluent exhibited increasing turbidity. When the column was back flushed after the run a large quantity of finely-divided, black, amorphous material was removed. This was found to contain a high concentration of magnesium, but only small amounts of the metals present in the feed solution.

GENERAL CONCLUSIONS

Our study of the silicon alloy system led to the following conclusions:

1. The primary reaction appears to be formation of hydroxide by reaction of the alkali component of the alloy with water, thus:

   $$Mg + H_2O \rightarrow MgO + H_2$$

   $$MgO + H_2O \rightarrow Mg(OH)_2$$

   In turn the magnesium hydroxide reacts with metal ions to form hydrous oxides or basic salts.

2. A reduction reaction also appears to take place, thus:

   $$3Mg + 2CrO_3 + 6H_2SO_4 \rightarrow 3MgSO_4 + Cr_2(SO_4)_3 + 6H_2O$$

   This reaction is probably inhibited by the rapid neutralization of the system.

3. There is no evidence that any constituent of the alloy other than the calcium or magnesium enters into the reaction.

4. The effectiveness of the alloys deteriorates before the bulk of the material is significantly diminished. We believe this to be a surface phenomenon, but have not determined whether it is due primarily to depletion of the active metal on the surface of the alloy granules or to formation of an inhibiting layer of reaction products. Vigorous stirring of the mixture of alloy granules and feed solution helps to prolong the effectiveness of the metal removal.

   In spite of the drawbacks of the system we believe alkali earth metal alloys and alloys of other metals with high oxidation potential offer an interesting area for further study.

SECTION VII

REFERENCES

1. Habashi, F., Principles of Extractive Metallurgy, Vol. 2 Hydrometallurgy, p. 235, Gordon and Breach, New York, N.Y. 1970.

2. Case, O. P., and Jones, R. B. L., "Treatment of Brass Mill Effluents", Conn. Research Commission RSA-68-34, Sept. 10, 1969.

3. Case, O. P., et al, "Method For Simultaneous Reduction of Hexavalent Chromium and Cementation of Copper", U.S. patent 3,748,124, Jul. 24, 1973.

4. Nadkarni, R. M.; Jelden, C. E.; Bowles, K. C.; Flanders, H. E.; and Wadsworth, M. E.; "A Kinetic Study of Copper Precipitation on Iron-Part I", Trans. Met. Soc. AIME, Vol. 239, Apr. 1967, p. 581.

5. Nadkarni, R. M., and Wadsworth, M. E., "A Kinetic Study of Copper Precipitation on Iron-Part II", Trans. Met. Soc. AIME, Vol. 239, Jul. 1967, p. 1066.

6. Rickard, R. S., and Fuerstenau, M. C., "An Electrochemical Investigation of Copper Cementation by Iron", Trans, Met. Soc. AIME, Vol. 242, Aug. 1968, p. 1487.

7. Strickland, P. [illegible], and Lawson, F., "Cementation of Copper With Zinc From Dilute Aqueous Solutions", Proc. Aust. Inst. Min. Met. No. 236, Dec. 1970, p. 25.

8. Levich, V. G., Physiochemical Hydrodynamics, Prentice Hall, Englewood Cliffs, N.J. 1962.

9. McKaveney, J. P.; Fassinger, W. P., and Stivers, D. A. "Removal of Heavy Metals from Water and Brine Using Silicon Alloys", Environ. Sci. and Tech., Vol. 6, No. 13, Dec. 1972, p. 1109.

10. McKaveney, J. P., "Process For the Removal of Ionic Metallic Impurities From Water", U.S. patent 3,766,036, Oct. 16, 1973.

11. Hoover, C. R., and Masselli, J. W., "Disposal of Waste Liquors from Chromium Plating", Ind. Eng. Chem., Vol. 33, No. 1, Jan. 1941, p. 131.

12. Back, A. E., "Precipitation of Copper from Dilute Solutions Using Particulate Iron," Jour. Met., May 1967, p. 27.

SECTION VIII

APPENDICES

		Page
A.	Experimental Procedure Utilized With Iron Shot as Reductant	33
B.	Experimental Procedures Utilized With Particulate Iron as Reductant	34
C.	Experimental Procedures Utilized With Alkaline Earth-Silicon Alloys as Reactant	35

APPENDIX A

EXPERIMENTAL PROCEDURE UTILIZED WITH IRON SHOT AS REDUCTANT

BATCH REACTION

1. Place 50 cc of freshly-cleaned shot, or combination of shot and glass beads, in reactor shown in Fig. 1.

2. Start flow of nitrogen at 2 liters/min. (initial experiments were carried out in air).

3. Add 100 ml of feed solution to reactor.

4. Rotate reactor at 30 to 60 RPM for 2 min.

5. Pour solution through a No. 5 filter paper.

6. Test the filtrate qualitatively for ferric iron. Determine pH and concentrations of iron and residual reducible ions (copper and hexavalent chromium).

7. Analyze the precipitate for copper and iron (in some cases).

8. Repeat using contact times of 4, 6, 8, 10, and 12 min..

CONTINUOUS (BACK-MIX) REACTION

1. Place 50 cc of freshly-cleaned shot, or combination of shot and glass beads in reactor shown in Fig. 1.

2. Start flow of nitrogen at 2 liters/min..

3. Fill the reactor to over flowing with feed solution (480 ml).

4. Rotate reactor at 30 RPM.

5. Pump feed solution through reactor at the rate of 25 ml/min. for 8 hours.

6. Following an initial period of 30 min., sample effluent over a 15-min. period at 30-min. intervals.

7. Analyze effluent for iron, residual copper and hexavalent chromium and determine pH.

APPENDIX B

EXPERIMENTAL PROCEDURES UTILIZED WITH PARTICULATE IRON AS REDUCTANT

LECO POWDER

1. Place 1 g of powder in a 250-ml beaker.
2. Add 100 ml of feed solution.
3. Stir with a mechanical stirrer at 500/700 RPM (rough estimate) for 2 min..
4. Decant solution and analyze for iron and copper and determine pH.
5. Rinse powder with distilled water and repeat steps 2 thru 4 using contact times of 4, 6, 8, 10, and 12 min..

HOEGANAES ACF POWDER

1. Add 100 ml of feed solution to a 250-ml separatory funnel connected to a source of nitrogen through the stem.
2. Add 0.05 g of powder (in the form of a well-mixed 1% suspension) and disperse the particles throughout the feed solution with a stream of nitrogen (0.8 liters/min.).
3. After a 2-min. contact time, pour the solution through a filter paper to remove iron particles.
4. Analyze the filtrate for copper and iron and determine pH.
5. Repeat steps 1 through 4, using contact times of 4, 6, 8, 10, and 12 min..

APPENDIX C

EXPERIMENTAL PROCEDURES UTILIZED WITH SILICON ALLOYS AS REACTANT

BATCH REACTIONS

Mixing By Stirring (Mg-Si Alloy)

1. Add 50 cc (78 g) of granules to a 300-ml Erlenmeyer flask.
2. Add 100 ml of feed solution to flask.
3. Stir for 5 min. with a 4.45 cm magnetic stirrer at approximately 200 RPM (rough estimate).
4. Filter solution and analyze filtrate for copper, zinc, chromium (T), chromium (+3) and magnesium and determine pH.
5. Using the same metal charge, add another 100 ml of feed solution and repeat steps 3 and 4.
6. Continue runs as in step 5 until 6 runs have been made.

Mixing By Tumbling (Mg-Si Alloy and Ca-Si Alloy)

1. Add 50 cc of granules to reactor shown in Fig. 1.
2. Add 100 ml of feed solution to reactor.
3. Rotate reactor at 45 RPM for 5 min.
4. Filter solution and analyze filtrate for copper, zinc, chromium (T), chromium (+3), and magnesium and determine pH.
5. Using the same metal charge, add another 100 ml of feed solution and repeat steps 3 and 4.
6. Continue runs as in step 5 until 6 runs have been made.

CONTINUOUS (PLUG-FLOW) REACTION

1. Place 50 cc (81.5 g) of 10/20 mesh Mg-Si granules in a vertical glass column 12.7 mm I.D. x 419 cm long.
2. Pump feed solution up through the packed column at a flow rate of 10 ml/min. for 90 min..

3. Collect effluent, replacing receiver every 15 min..

4. Analyze each portion of effluent for copper, zinc, chromium (T) and determine pH.